



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

REC'D 21 NOV 2003

WIPO

PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02079617.3

18/03/4693

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr:
Application no.: 02079617.3
Demande no:

Anmeldetag:
Date of filing: 05.11.02
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Koninklijke Philips Electronics N.V.
Groenewoudseweg 1
5621 BA Eindhoven
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Nanostructure electronic device therewith and method of preparing the same

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

H01L21/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

Nanostructure, electronic device therewith and method of preparing the same

The invention relates to a nanostructure of an inorganic semiconductor material.

The invention also relates to a dispersion of nanostructures in a solvent.

5 The invention further relates to an electronic device comprising a first and a second electrode that are mutually connected through at least one nanostructure.

The invention further relates to a method of preparing nanostructures of an inorganic semiconductor material, comprising the steps of:

10 providing growth nuclei of an electrically conducting material on a electrically conductive surface of a substrate; and
growing the nanostructures by chemical vapour deposition at a growth temperature.

The invention further relates to a method of manufacturing an electronic device, comprising the steps of:

15 providing growth nuclei of an electrically conducting material on a electrically conductive surface of a substrate, the surface being patterned so as to define a first electrode;
growing nanostructures of a compound semiconductor material by chemical vapour deposition at a growth temperature; and
20 providing a second electrode that is in electrical contact with the nanostructures grown.

25 A semiconductor Light-Emitting Diode (LED) is known in the art. Such a LED comprises a superlattice of active layers. Such superlattices are typically generated by the epitaxial growth of multi-layer active crystals separated by barrier layers. A problem with superlattices is that they are relatively expensive and difficult to produce and the fabrication of superlattices is limited to several material systems including group III-V and group II-VI compounds.

The wavelength of the light emitted by a LED is determined by the bandgap of the semiconductor used. To obtain a high efficiency (electron-photon conversion) a direct

bandgap material should be used. For the red ($600 < \lambda < 900$ nm) region in the electromagnetic spectrum several, direct bandgap, compound semiconductors, such as AlGaAs, could be used. The efficiency for red-emitting LEDs could be as high as 90%. For the blue ($\lambda \sim 450$ nm) a compound direct-bandgap semiconductor such as GaN could be used, and for the green
5 (($\lambda \sim 520$ nm) InGaN could be used. However, the efficiency of LEDs emitting wavelengths below 600 nm is low ($\sim 10\%$). The problem, resulting in such low efficiencies, is that the compound (In)GaN material is not mono-crystalline. Non-crystallinity leads to defect states in the bulk of the material. A high concentration of defect states causes radiationless transitions. Also the mobility of the charge carriers is decreased by the high concentration of
10 defects.

Another approach to make a LED is by using semiconducting, single-crystalline nanowires. Compound semiconducting nanowires of the groups II-VI and III-V of the Periodic Table, as well as nanowires of the group IV of the Periodic Table (i.e. silicon) have been synthesised by using the Vapor-Liquid-Solid (VLS) method. The diameter of the
15 wires is in the range 5-50 nm. In this range, the physical dimensions of the material may have a critical effect on the electronic and optical properties of the structure. Quantum confinement refers to the restriction of the electronic wave function to small regions of space within a particle of material referred to as the resonance cavity. Semiconductor structures of which all three dimensions are in the nanometer size range are typically referred to as
20 quantum dots. When the quantum confinement is in two dimensions, the structures are typically referred to as a one-dimensional quantum wire or more simply as quantum wire or nanowire. A quantum wire thus refers to a wire having a diameter sufficiently small to cause confinement to directions normal to the wire. Such two-dimensional quantum confinement changes the wire's electronic properties.

25 C.M. Lieber and coworkers - *Nature* 2002, 415, 617-620 - and K. Hiruma and coworkers - *Appl. Phys. Lett.* 1992, 60, 745-747 - have shown that it is possible to synthesize InP and GaAs quantum wires, respectively, which contain a p-n junction. Electroluminescence was observed when a forward bias was applied to the device. Holes are injected in the p-type part of the wire and electrons in the n-type part of the wire. At the p-n
30 junction the electrons and holes recombine and as a result light is emitted. The emitted light was polarized. The efficiency (electron-photon conversion) was not high (0.1 %). This might be due to surface defect states. No attempts were done yet to passivate the surface of these III-V materials with established methods. An anneal step in 1 % H₂S in H₂ at 300°C could passivate the surface with sulfur groups increasing the luminescence by a factor of 10-100.

Hiruma and coworkers showed that the blueshift of the electroluminescence from the wires, having a diameter of 60 nm, with respect to bulk emission was very small (10 meV). In the work of Lieber and coworkers the blue shift was not quantitatively mentioned. From photoluminescence measurements by Lieber and coworkers on wires with different diameters it was shown that for wires having a diameter of 10 nm the blueshift was 110 meV with respect to bulk emission.

It is a disadvantage that such a blueshift is still rather small. The standard wavelength of InP for instance is in the infrared spectrum, and the observed blueshift are not enough to provide light with wavelengths.

It is thus a first object of the invention to provide nanostructures with a larger blueshift. It is a second object of the invention to provide devices comprising such nanostructures which devices are able to emit radiation in the visible spectrum.

This first object is realized in that the nanostructure comprises a nanotube with a crystalline mantle and a hollow core. Unexpectedly, it has been found that such tubes are formed with a cylindrically shaped crystalline mantle and that they are stable. In the experiments done, the crystal structure was found to be equal to the bulk crystal structure and particularly of the diamond, zinc blende or wurtzite structure. The nanotubes thus formed were mechanically and chemically stable; the tubes did not oxidize upon exposure to ambient air during a week. Further on, the nanotubes could be synthesized as an ensemble of structures all having substantially the same electronic properties.

Even more unexpectedly, it was found that the nanotubes show a much larger blueshift of the emission wavelength than nanowires of a compound semiconductor material. This large blueshift is attributed to comparatively thin diameters of the mantle resulting in a larger quantum confinement of the electronic wave functions.

Photoluminescence measurements have shown that the blueshift for InP nanotubes having a diameter of 10 nm and a wall thickness of 3 nm is 800 meV; e.g. the tubes show photoluminescence at a wavelength of 580 nm upon excitation at 514 nm; this indicates that neither surface states nor bulk trap states dominate the electronic properties, for which thus the geometric structure appears responsible. This blueshift is such, that light emission in the visible spectrum is possible based on electroluminescence. Various desired wavelengths in the entire range of the visible spectrum can be obtained through the choice of the material of the compound semiconductor material, such as InP, GaAs, AlGaAs, GaP, and through the choice and concentration of the dopant, such as S, Se, Te, Zn. It may further be, that the nanostructure comprises different materials in different regions.

Nanotubes of other materials, such as carbon and transition metal chalcogenide are known per se. However, these nanotubes have a pseudographitic structure, and the electronic properties are determined by the diameter of the tube and the chirality. It is difficult to dope such nanotubes with a suitably dopant, and it is thus difficult if not impossible to obtain light-emitting behaviour. Beyond that, it is impossible to fabricate an ensemble of these nanotubes, such that all nanotubes have the same electronic structure.

Preferably, overall diameter of the nanotube is in the range of 1-100 nm. The hollow core of the nanostructure has a diameter in the range of 2-20 nm by preference. The crystalline mantle has a diameter in the range of 0.5-20 nm by preference.

The nanotube structure may extend over the complete length of the nanostructure. Alternatively, it is limited to a region in the nanostructure, while in other parts of the nanostructure a nanowire structure or a partially filled nanotube structure is present. Such a limitation of the nanotube to a region can be advantageously realized by variation of the growth temperature in a chemical vapour deposition growth process. The limitation has the advantageous effect that the light excitation of a desired material takes place at a specific location. Besides, this dot-structure has an even larger quantum confinement than a complete nanotube. Further on, the nanowire region that may have a larger diameter, allows improvement of the mechanical stability. Such mechanical stability is particularly important if the nanostructures are to be provided in a dispersion onto a surface, and particularly, wherein electrical contact must be established to electrodes, for instance of Au.

In a further embodiment, the nanostructure comprises a first zone having a p-type doping and a second zone having an n-type doping, the first and second zone having a mutual interface constituting a pn-junction. Due to the provision of a pn-junction in the nanostructure, electroluminescent effects are obtained. If desired, the nanostructure can contain two p-n-junctions as well, thus leading to a bipolar transistor.

The second object is realized in an electronic device comprising a first and a second electrode that are mutually connected through at least one nanostructure that comprises a nanotube with a crystalline mantle and a hollow core. It is particularly preferred that the nanostructure comprises a first zone having a p-type doping and a second zone having an n-type doping, the first and second zone having a mutual interface constituting a pn-junction. Herewith a light-emitting diode is obtained, in which the first electrode functions as a hole-injecting electrode and the second electrode as an electron-injecting electrode. Such light-emitting diode can for instance be used for display and lighting applications, as is

known per se. However, the device with the nanotubes having a large quantum confinement and a suitable electroluminescent and photoluminescent effect is suitable as well for memory purposes (e.g. quantum dots), for ultrafast transistors and for optical switches, optocouplers and photodiodes (to convert an optical signal into an electrical signal or to do the reverse).

5 The device of the invention can have various forms. It is advantageous if the nanostructures are present in an array within a layer, this layer separating the first and the second electrode. In this embodiment, the nanostructures are directed substantially transversal to electrodes. Advantages of this "vertical" type of device include that no assembly of the nanostructures is necessary and that an array of nanostructures can be used
10 for interconnecting both electrodes.

 The layer in which the nanostructures are present, can be provided before the growth of the nanostructures, e.g. as a porous matrix of for instance alumina. However, it can be provided as well afterwards, e.g. by growing the nanostructures and providing the layer from solution afterwards. A very suitable manner of providing such layer is sol-gel
15 processing. A particularly advantageous layer comprises a mesoporous silica which may contain organic substitutions. Such a layer has a low dielectric constant, which reduces undesired capacitive interaction between the first and the second electrode. Alternatively, a polymer can be used, that is transparent if optical properties of the nanostructures are to be exploited. This has the advantage that a flexible device can be obtained.

20 The array type of device is particularly suitable in combination with a nanostructure including a p-n-junction. Such an array will result in a very high light output power density. If the array has a density of 10^{10} pores and hence nanostructures per cm^2 , the power density can be in the range of 10^2 - 10^4 W/cm^2 . Further on, due to the crystallinity of the nanostructures, the efficiency of the light emitting diode is high, for instance about 60 %.

25 In the case that a bipolar transistor in the nanostructure is desired, this can be realized with the matrix containing internal conductors, or in that a conductive layer is provided between two sublayers after growing the nanostructures. Also the growing of the nanostructures may be done in steps such that after a first growth step, a first sublayer is provided. Then the conductor can be deposited, whereafter the growth process is continued in
30 a second growth step, with the same metal nuclei. In order to improve the contact between such internal conductor and the nanostructure, it is preferred that the nanostructure has a mantle with a larger diameter or is a nanowire with a larger diameter at the contact with the internal conductor.

The layer may further be structured according to a desired pattern. This is particularly advantageous, if the nanostructure is used as a photodiode. In that case, the layer can be structured so as to have a fiber-like shape. Around the structured layer black or non-transparent layers can be provided, so as to keep the light inside the layer.

5 In a further embodiment, the layer contains nanostructures of different materials. Herewith a multicolor light-emitting device is realized. The nanostructures of different materials can be provided in that a plurality of growth cycles is done, with first the provision of the nuclei, generally a droplet of a metal and then the growth at one or more desired growth temperatures, and then the removal of the nuclei, so as to stop the growth.

10 If used as a light-emitting diode, at least one of the electrodes is preferably transparent. At the side of the layer opposed to the transparent electrode, a reflecting layer may be present, so as to enlarge the efficiency of the light output.

Nonetheless the advantages of the vertical device type, the nanostructures of the invention may be present in a thin-film device type, wherein the first and second
15 electrode are laterally spaced apart. A dispersion with the nanostructures, for instance in ethanol as dispergent, is then provided onto the electrodes. The alignment of the nanostructures and the electrical contacting between electrodes and nanostructures can be realized in per se known manner, as is also disclosed by Lieber and coworkers.

20 It is a third object of the invention to provide methods of the kind described in the opening paragraph with which the nanostructures can be suitably and easily made.

This is realized in that the growth temperature is above a transition temperature, therewith obtaining nanotubes. Below this transition temperature nanowires or partially filled nanotubes are obtained. The transition temperature depends on the type and
25 the concentration of dopants. It lies around 500 °C for InP. If desired, the nanotubes obtained can be thinned by oxidation. However, due to further increase of the temperature the thickness of the mantle can be reduced adequately.

The nuclei used as growth catalysts in the method of the invention are chosen from a suitable metal or a colloidal particles including such metal. Examples of suitable
30 metals are Co, Ni, Cu, Fe, In, Ga, Ag and Pt.

These and other embodiments of the nanostructure, the device, and the methods of the invention will be further explained to the figures and tables, in which:

Fig. 1 shows a first embodiment of the method of preparing the nanotubes;

Fig. 2 shows Electronmicroscopy images of the nanotubes;

Table 1 shows data regarding the transition temperature;

Fig. 3 shows a plot of the mantle thickness d (nm) of a InP nanotube versus the
5 substrate temperature T ($^{\circ}\text{C}$);

Fig. 4 shows a figure wherein the intensity I of emission is shown for InP
nanotubes (graph A), InP nanowires (graph B), and InP nanotubes (graph C) as function of
the wavelength λ ;

Fig. 5 shows TEM images of a partly hollow InP tube induced by dopant
10 atoms;

Fig. 6 shows TEM images of a partly hollow InP tube with diameter variations
induced by a temperature modulation;

Fig. 7 shows a first embodiment of the method of manufacturing the electronic
device;

Fig. 8 shows a second embodiment of the method of manufacturing the
15 electronic device; and

Fig. 9 shows a third embodiment of the method of manufacturing the
electronic device.

20

The figures are schematical and not drawn to scale. Like reference numbers in
different figures refer to the same or similar parts. The figures and the description are merely
examples and should not be considered to set the scope of the present invention.

25 Embodiment 1

InP nanotubes were synthesised with the VLS growth method, in analogy to
semiconducting nanowires, but at higher temperatures. A silicon substrate provided with an
oxidized surface ("native oxide") and thereon a thin (2-10 Å) Au film was placed on an
Al₂O₃ block in a tube oven at the downstream end. The substrate temperature was measured 1
30 mm below the substrate in the Al₂O₃ block. The oven is evacuated to less than 10 Pa.
Thereafter, the pressure is set to $3 \cdot 10^{-4}$ Pa with a 100-300 sccm flow of Ar. The oven is heated
to 500 $^{\circ}\text{C}$ resulting in the splitting of the Au layer into clusters on the scale of nanometers. At
the upstream end of the oven an InP target (density 65%) is positioned and with an ArF laser
($\lambda = 193$ nm, 100 mJ/pulse, 10 Hz) the InP is ablated from the target. The InP is vaporized

and transported over the substrate. This results in the growth of nanostructures under the catalysis of the Au-clusters.

Fig. 1 shows schematically the temperature dependent growth of the nanostructures. At relatively low substrate temperatures ($<500^{\circ}\text{C}$) the wire growth is limited by the crystal growth rate at the liquid-solid interface. The semiconductor species are homogeneous distributed throughout the liquid droplet and a solid semiconducting nanowire is formed. At higher substrate temperatures ($>500^{\circ}\text{C}$) the reaction becomes diffusion limited; the diffusion of semiconducting species through the liquid droplet is relatively slow compared to crystal growth. The concentration of the semiconductor species becomes depleted and due to geometry reasons the crystal growth starts circularly. As a results nanotubes, having a crystalline mantle and a hollow core, are formed. The applied substrate temperature determines the overall diameter of the tube and the mantle thickness.

Fig. 2 shows SEM and TEM images of InP nanotubes grown at 515°C on a silicon substrate. The SEM images were made with a Philips XL40FEG apparatus. The TEM images were made with a TECNAI TF30ST apparatus. Fig. 2a shows a SEM image. From this SEM image it is clear that over 95 % of the deposited material consisted of wire-like structures. Fig. 2b and 2c show TEM images. This allows a closer examination that reveals that hollow tubes were formed. Judging from the contrast from both bright field TEM and HAADF (high-angle annular dark field) imaging it was clear that there was no material present in the core of the tubes. As can be seen in Fig. 2c, the tubes were terminated by a spherical particle which contained gold. This indicates that the tubes grow from the liquid InP-Au phase via the VLS mechanism. The diameter of the tubes was uniform along its length.

Fig. 2d and 2e show TEM image of a further InP nanotube, which was doped with Zn and grown at 520°C . In Fig. 2 a darker contrast in the mantles – also called walls – of the tube is present. This is a diffraction contrast originating from the crystalline nature of this tube. Upon tilting the sample with respect to the electron beam diffraction contrast fringes can be seen to move over the entire width of the tubes, implying a cylindrical shape of the crystals. The observation that the diffraction contrast is most pronounced in the walls again confirms the hollow nature of the tubes. The thickness of the wall of the nanotube shown in the HRTEM image (figure 2(e)) was approximately 4 nm. The crystal lattice corresponded to the InP zinc blende lattice and the tubes were grown in the $[200]$ direction. The tubes did not oxidize upon exposure to ambient air for a week.

Fig. 3 shows a graph of the mantle thickness d versus the substrate temperature T , for the nanotubes prepared as mentioned above. The thickness decreases from about 14 to 9 nm while increasing the temperature from 490 °C to 550 °C. At about 500 °C the transition from nanowires to nanotubes takes place. This is found back in the graph in that the decrease in thickness is relatively steep around this transition temperature.

Fig. 4 shows a diagram wherein the intensity of the light emission is set out against the wavelength λ in nm. Three graphs are shown: one for InP nanotubes (graph A), one for InP nanowires (graph B) and one for Bulk InP (graph C). The data for the nanotubes are based on the nanotubes obtained as described above, with a mantle thickness of 4 nm. The data for the nanowires are based on nanowires with a diameter of 5 nm which were prepared with the VLS method at a temperature below 500 °C. The measurement are photoluminescence measurements, wherein the samples were irradiated with a Ar laser with a wavelength of 514nm. As is clear from this figure, the emission of the nanotubes takes place at a wavelength that is remarkably much smaller than the wavelength of the InP nanowires and of bulk InP. Particularly, the emission of the nanowires has blueshifted 150 nm (250 meV) with respect to the bulk emission. The emission of the nanotubes has blueshifted 310 nm (750 meV) with respect to bulk emission.

Embodiment 2

In further embodiments, the growth experiments were repeated. Herewith the targets were changed, so as to contain dopant atoms. In this manner the nanotubes were electrically doped to form p-type and n-type semiconductors. However, the added dopant influences the growth dynamics of the nanotubes. In the presence of dopants a different morphology, *i.e.* nanotubes partly filled with InP crystallites, was also observed. The obtained morphology depended on the dopants added to the InP target and on the substrate temperature.

Fig. 5 shows TEM images of such partially filled nanotubes. Figure 5(a) shows a TEM image of a partly hollow tube formed by using an InP target doped with 0.1 mol% Zn at a substrate temperature of 467°C. Figures 5(b) and (c) show HRTEM images of the location where the crystalline core is interrupted. The crystallographic orientation is identical at both sides of the gap. With static SIMS and XPS it was semi-quantitatively shown that dopant atoms were transferred from the target into the wires. When a target dopant concentration of 1.0 mol % with respect to InP was used an estimated concentration of 10^{20} atoms/cm³ was present in the wires.

Table 1 shows the obtained morphology when dopants (0.1 or 1 mol %) were added to the target at a given temperature. The target dopant concentration had no influence on the resulting morphology. At the higher temperatures tubes were formed and at the lower temperatures solid wires. At intermediate temperatures the partly filled tubes were observed.

5

Table 1. The obtained morphology in the indicated substrate temperature range when a dopant was added to the InP target.

Dopant	Solid wire	Partly filled	Hollow tube
No dope	$T < 500^{\circ}\text{C}$	-	$T > 500^{\circ}\text{C}$
S	-	$460 < T < 480^{\circ}\text{C}$	$T > 480^{\circ}\text{C}$
Se	$T < 485^{\circ}\text{C}$	$485 < T < 530^{\circ}\text{C}$	$T > 530^{\circ}\text{C}$
Te	$T < 500^{\circ}\text{C}$	no data	No data
Zn	$T < 450^{\circ}\text{C}$	$450 < T < 515^{\circ}\text{C}$	$T > 515^{\circ}\text{C}$

10

Embodiment 2

Fig. 6 shows an embodiment of the present device 10 comprising a light-emitting diode. The device 10 comprises a substrate 10, on which a first electrically conductive layer is present in which the first electrode 2 is defined. The substrate 1 is in this case of insulating material, e.g. Al_2O_3 and the conductive layer comprises Ti in this example. The conductive layer 2 is connected to pixel switches and a driver circuit that are not shown. However, these pixel switches, for instance transistors of polysilicon or amorphous silicon, can be provided in the substrate 1. On the first electrode 2 a porous matrix 3 is present, of which the pores are filled with nanotubes 4 of InP having a first region 5 that is p-type doped with a first dopant of Se and a second region 6 that is n-type doped with a second dopant of Zn. A p-n-junction is present at the mutual interface 7 of the first and the second region 5,6. At the upper surface 14 of the porous matrix a second, transparent electrode 8 of ITO is present. This stack constitutes the light-emitting diode. By preference, a plurality of light emitting diodes is present on the substrate 1, as the skilled person will understand.

25

The diode is manufactured as follows. After provision of the first electrode 2 by sputtering of a layer of Ti a matrix 3 of porous anodic alumina was provided. It had a thickness of 0.2 micrometers and a density of pores of 10^{10} pores/cm³. These pores, each with

a diameter of 20 nm, were vertically aligned. The alumina matrix 3 was manufactured as described in accordance with the method described in WO-A 98/48456.

Nucleus particles, in this example of Au, were then electrochemically deposited at the bottom of the pores. This substrate 1 with the porous matrix 3 was placed in an oven. At the upstream end of the oven an InP target is positioned and with an ArF laser the InP is ablated from the target. The InP is vaporized and transported over the substrate. This results in the growth of nanostructures under the catalysis of the Au-clusters. A first region 5 of the nanotube is grown with a n-type dopant, in this case Se at a temperature of 550 °C. After that the first region had been grown with a length of 100 – which however may be longer or shorter -, the gas composition is changed, and the Se dopant is replaced by a Zn dopant. A second region 6 is grown with this composition, with a length of 120 nm. The first and second region 5,6 have a mutual interface 7, at which a p-n-junction is present. The upper surface 14 of the matrix 3 is now slightly polished, so as to remove the nucleus particles and the protruding parts of the nanostructures. Thereafter, a layer of indium-tin-oxide (ITO) is deposited in the known manner so as to provide the second electrode 8.

Embodiment 3

Fig. 7 shows schematically and in cross-sectional view three steps in the method of the invention. Fig. 7A shows a substrate 10 comprising a carrier 1 of borosilicate glass. Thereon, an electrically conductive layer 2 is present, which comprises Al. Nanotubes 3 are grown thereon, in a hot film chemical vapour deposition reactor at 550 °C, with nuclei 11, in this case of Au. The nanotubes 4 are grown up to a length of 100-200 nanometers and a diameter of about 10 nanometers.

Fig. 7B shows a second step. Therein a layer of a solution of 2,1 g lead acetate, 9,3 g tetraethoxysilane, 1,9 g trimethylborate and 1,0 triethylaluminate in 80 g ethanol and 10 g acidified water (1 N HCl) was prepared. After hydrolysing for one hour, the solution is provided on the substrate by means of spincoating. The sol-gel layer provided by spincoating was converted to a glass composition comprising 52.7 wt% SiO₂, 6.4 wt% Al₂O₃, 13.0 wt% B₂O₃ and 27.9 wt% PbO by heating at 300 °C for 45 minutes. The glass is thermally stable to at least 250 °C, which may be advantageous for other process steps. The glass composition may be modified, so as to prevent substantial differences between the thermal expansion of the nanotubes and the glass. The thickness of the obtained solid matrix 4 was 200 nm. Subsequently, the resulting structure is cooled to room temperature. To obtain a layer with a larger thickness, the tetraethoxysilane can be replaced partially by

trimethylmethoxysilane and oxidic nanoparticles (silicasol having a solids content of 50%; ludox) are added.

Fig. 7C shows the result of a third step, in which the matrix 4 with the nanotubes 3 is polished, so as to expose the ends of the nanotubes 4. The thickness of the matrix is chosen to be between about 150 nm, so as to provide a sufficient aspect ratio. The polishing results in a uniform surface 14. In order to assure that the ends of the nanotubes 4 are effectively exposed, and not hindered by glass particles, the surface 14 is cleaned after the polishing.

10 Embodiment 4

Fig. 8 shows schematically a diagrammatical cross-section of a semiconductor device 100, which is a thin-film-transistor in this case. On a substrate 110 of glass a source electrode 101 and a drain electrode 102 are provided. The electrodes 101,102 comprise Au, for example, and have been defined photolithographically. Other metals such as Al/Ti or Au/Ni/Ge can be used as well. The electrodes 101,102 are mutually separated by a channel 105, which comprises a dielectric material, with a low dielectric constant by preference. Suitable materials are known to the skilled person and include silicon oxide, hydrogen- and methylsilsesquioxane, porous silica, SiLK and benzocyclobutene. The choice of the material is also dependent on the choice of the substrate. The surface 111 of the electrodes 101, 102 and the channel 105 is planarized, so as to provide the nanostructures 4 on an essentially flat surface 111.

The nanostructures have been manufactured in accordance with Embodiment 1. After immersing the substrate with the nanotubes in a bath of a dispersant, it is ultrasonically vibrated during 2 seconds. As a result hereof, the tubes are dispersed. The dispersant is in this case ethanol, but may for instance be isopropanol, chlorobenzene or water as well, or mixtures thereof. Hereafter, a droplet of the dispersion is applied on the surface. Alignment of the nanotubes took place with a technique called flow assembly, wherein a stamp having a stamp surface with desired patterns, including a microfluidic channel, is provided on the substrate 111. Hereafter, an annealing step was done to improve the contact between the electrodes 101,102 and the nanotubes 10.

Hereon, a dielectric layer 106 is present, which separates gate-electrode 103 from the nanostructures 10. Therewith the transistor is complete. As will be clear to the skilled person, the electronic device comprises a plurality of transistors and/or other semiconductor elements, such as memory cells and display pixels, by preference. As will be

clear as well, other constructions of semiconductor devices, thin film transistors in particular, may be provided instead of the shown field-effect transistor, including the construction of a horizontal light-emitting diode.

Particularly, if the substrate comprises a semiconductor material, such as
5 silicon, this may be adequately doped to act as gate-electrode, and be provided with an oxide to act as gate oxide material. Preferably, a small channel length, preferably in the order of 0.1-0.3 μm is applied. In this manner, single charge carriers can be put onto the inorganic semiconductor nanotubes, at suitable temperatures, e.g. 77 K and higher. This can be done with excellent result, which is due to the enhanced confinement effect of the nanostructures
10 of the invention, and the reduced self capacitance resulting from the small channel length. A further advantageous effect is obtainable when using nanotubes having cores that are partially filled with crystallites. The confinement effect is less in these crystallites, leading to charge concentration therein. Thus, the crystallites will act as a quantum well. This quantum well does not only have advantageous effects for storage purposes, but also as a recombination
15 centre acting as light emitter. In this manner, the light emitting behaviour can be further tuned even without the provision of different materials.

CLAIMS:

1. A nanostructure of an inorganic semiconductor material, characterized in that the nanostructure comprises a nanotube with a crystalline mantle and an hollow core.
2. A nanostructure as claimed in Claim 1, characterized in that the hollow core
5 has a diameter in the range of 2 and 20 nm.
3. A nanostructure as claimed in Claim 1 or 2, characterized in that the mantle has a thickness in the range of 1-20 nm.
- 10 4. A nanostructure as claimed in Claim 1, characterized in that the hollow core is partially filled with the compound semiconductor material of the mantle of the nanotube.
5. A nanostructure as claimed in Claim 1, characterized in that the nanostructure comprises a first zone having a p-type doping and a second zone having an n-type doping, the
15 first and second zone having a mutual interface constituting a pn-junction.
6. A nanostructure as claimed in Claim 1, characterized in that the inorganic semiconductor material is chosen from the group of III-V semiconductor materials.
- 20 7. A dispersion of nanostructures according to any of the Claims 1-6 in a solvent.
8. An electronic device comprising a first and a second electrode that are mutually connected through at least one nanostructure according to any of the Claims 1-6.
- 25 9. An electronic device as claimed in Claim 8, characterized in that an insulating substrate with pores that are mutually substantially parallel is present, the pores extending from the first to the second electrode, in which pores the nanostructures are provided.

10. A method of preparing nanostructures of a compound semiconductor material, comprising the steps of:

providing growth nuclei of an electrically conducting material on a electrically conductive surface of a substrate; and

5 growing the nanostructures by chemical vapour deposition at a growth temperature,

characterized in that the growth temperature is above a first transition temperature during a first growth period, therewith obtaining nanotubes having a crystalline mantle and a hollow core.

10

11. A method as claimed in Claim 10, characterized in that the thickness of the mantle is varied by variation of the temperature above the first transition temperature.

12. A method of manufacturing an electronic device, comprising the steps of
15 providing growth nuclei of an electrically conducting material on a electrically conductive surface of a substrate, the surface being patterned so as to define a first electrode; growing nanostructures of a compound semiconductor material by chemical vapour deposition at a growth temperature; and

20 providing a second electrode that is in electrical contact with the nanostructures grown,

characterized in that the growth temperature is above a first transition temperature during a first growth period, therewith obtaining nanotubes, having a crystalline mantle and a hollow core.

25 13. A method of manufacturing as claimed in Claim 12, characterized in that during the growth first a first dopant is added to the vapour in the chemical vapour deposition reactor and thereafter a second dopant is added, the first dopant being of a first doping type and the second dopant being of a second doping type.

ABSTRACT:

The compound nanotubes of InP or another II-VI or III-V material show a very large blueshift. Thus, devices with photoluminescent and electroluminescent effects in the visible range of the electromagnetic spectrum are provided by the inclusion of such nanotubes.

5

Fig. 1

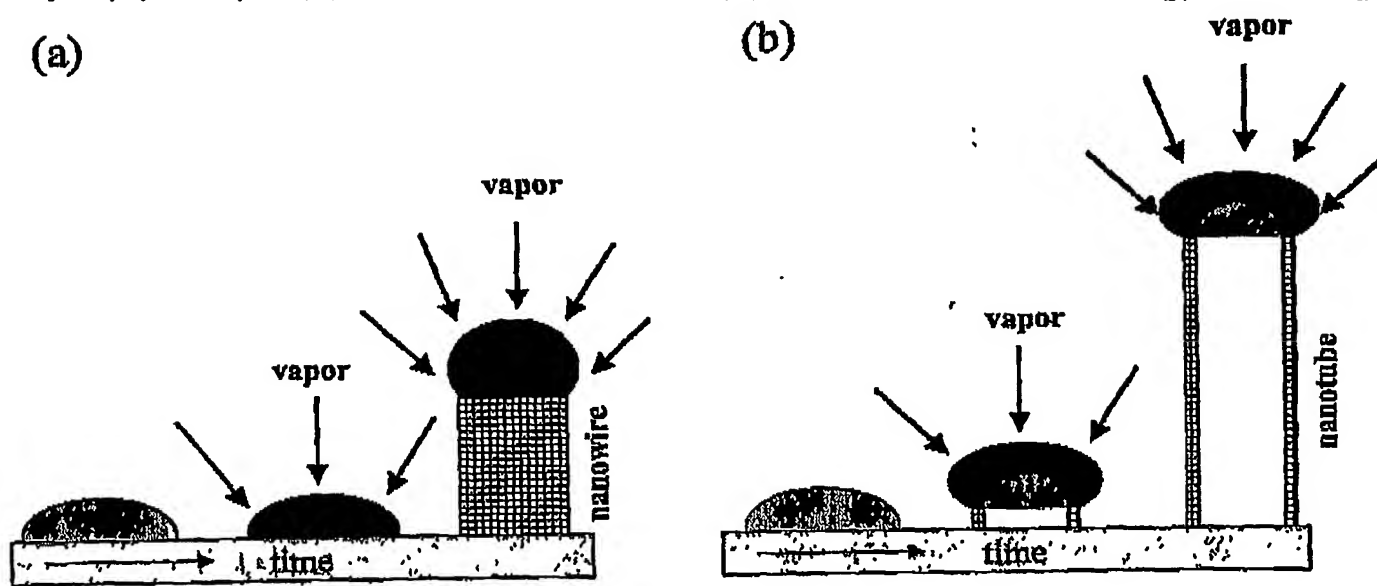


Fig 1

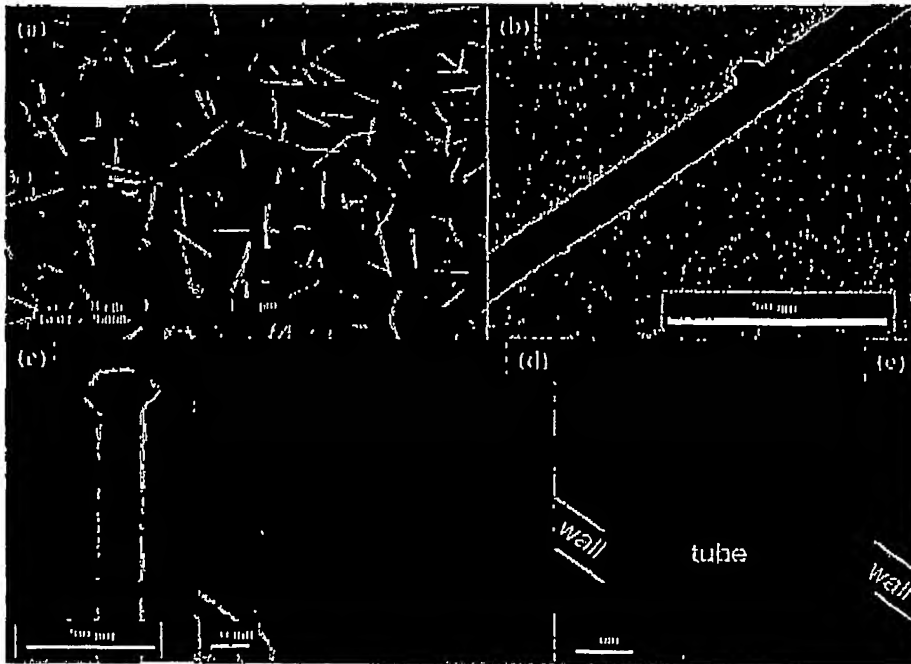


Fig. 2 A-E

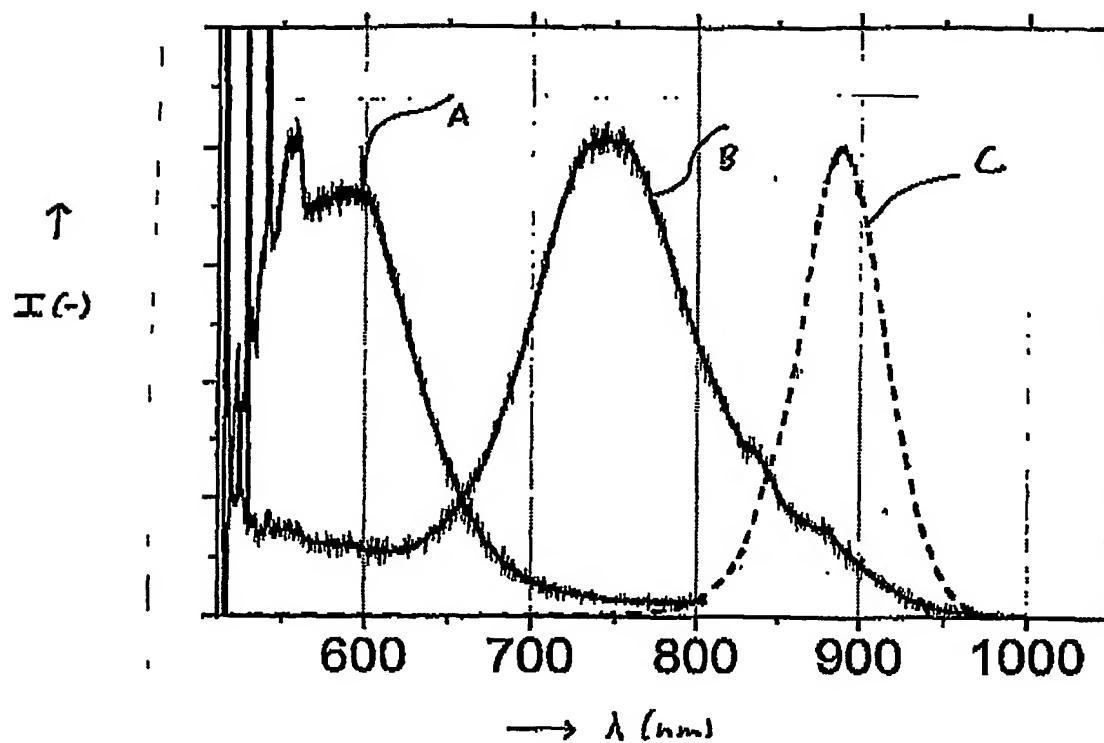


Fig 4

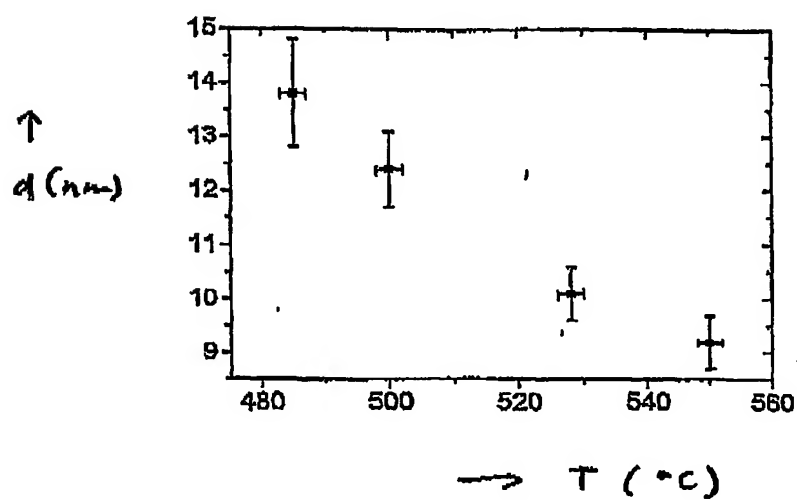


Fig 3

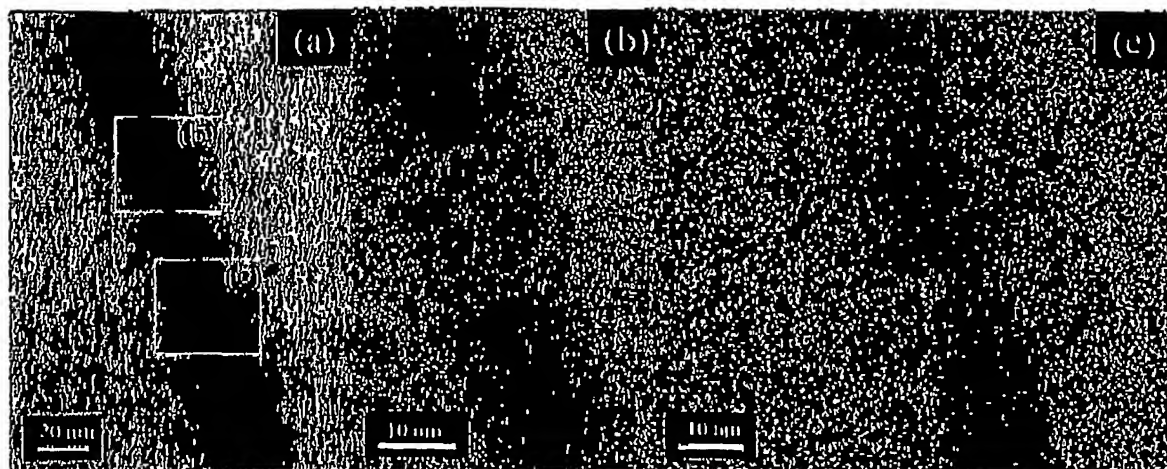


Fig. 5 A-C

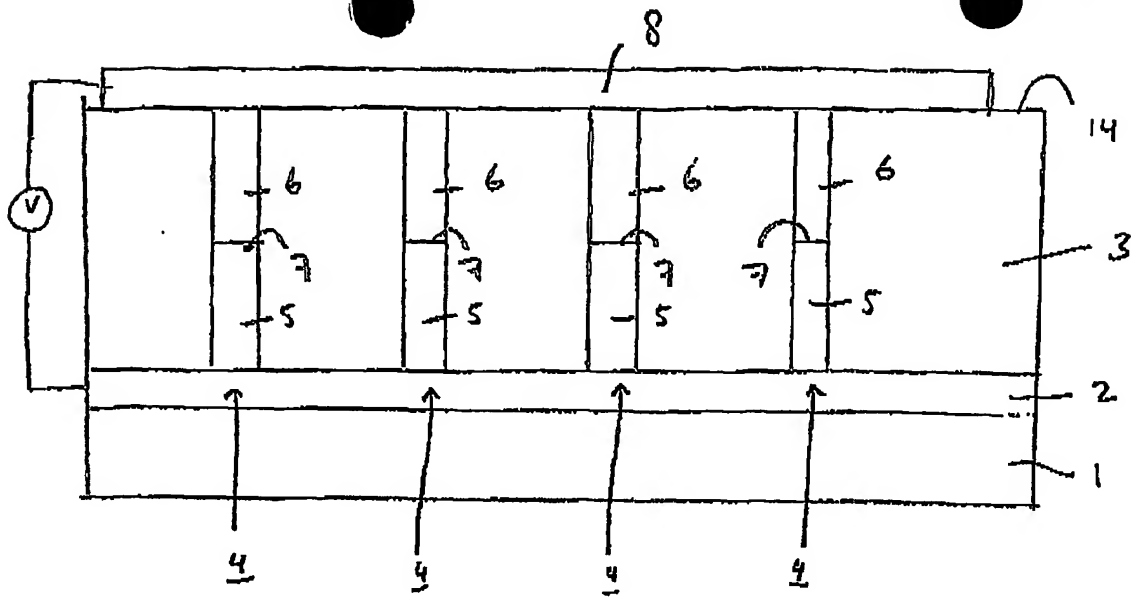


Fig 6

1/2

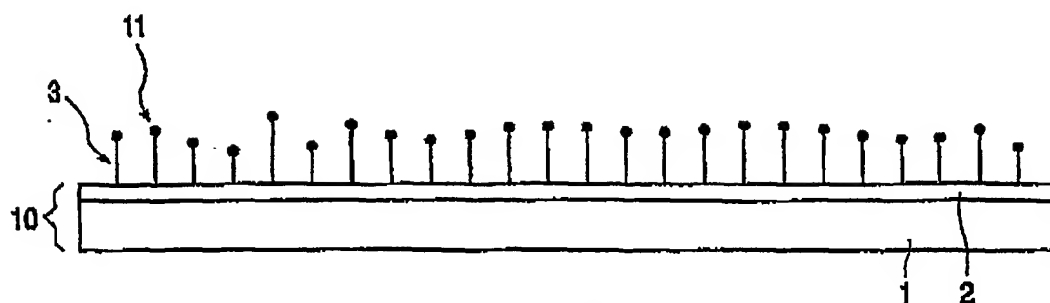


FIG. 1A 7A

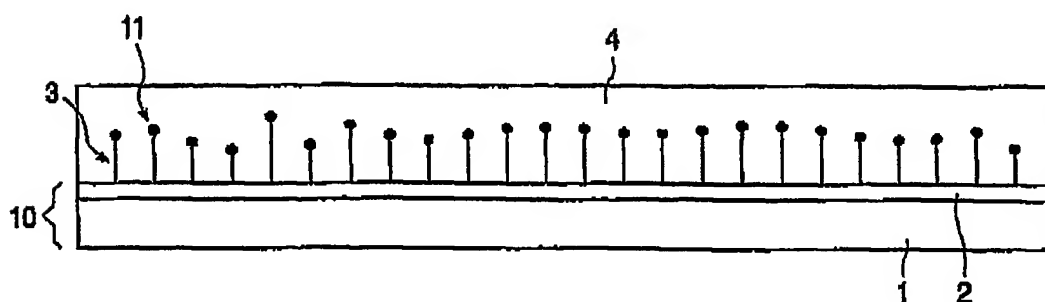


FIG. 1B 7B

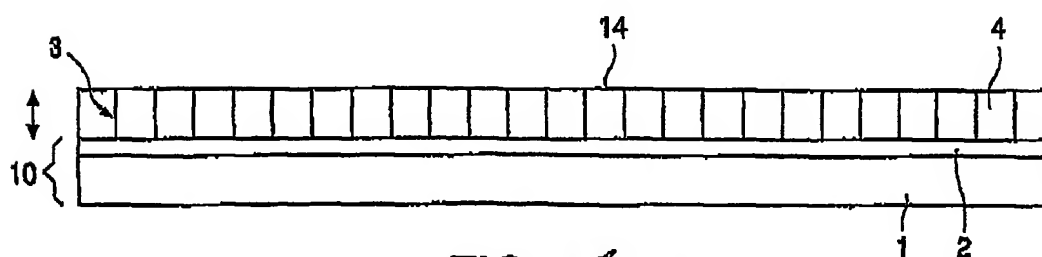
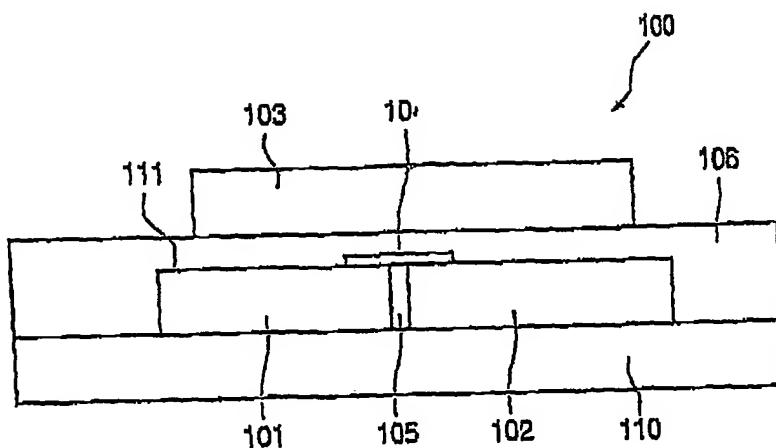


FIG. 1C 7C

Fig 8



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.